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Nonionic Surfactant Adsorption at the Ethylammonium Nitrate Surface: A Neutron Reflectivity and Vibrational Sum Frequency Spectroscopy Study

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Abstract

The adsorbed layers of polyoxyethylene n-alkyl ether surfactants $C_{12}E_4$, $C_{14}E_4$ and $C_{16}E_4$ at the EAN surface have a head group layer that is thin and compact (only ~30% EAN by volume). The headgroups do not adopt a preferred orientation and are disordered within the ethylene oxide layer. Alkyl tails contain a significant number of gauche defects indicating a high degree of conformational disorder. The thickness of the tail layer increases with increasing alkyl chain length, while the headgroup layer shows little change. Lowering the $C_{12}E_4$ concentration from 1 wt% to 0.1 wt% decreases the adsorbed amount, and the headgroup layer becomes thinner and less solvated, whereas $C_{14}E_4$ and $C_{16}E_4$ adsorbed layers are unaffected by dilution over the same concentration range. The $C_{16}E_4$ layer thickness increases and area per molecule decreases on warming to 60°C, but the adsorbed layer structures of $C_{12}E_4$ and $C_{14}E_4$ are unchanged. Both effects are attributed to surfactant solubility.

1. Introduction

Room temperature ionic liquids (ILs) are attracting a great deal of attention in a variety of areas. Much of this arises from the ease with which physiochemical properties such as viscosity, conductivity, and polarity, can be controlled through the careful selection of the cation and anion,^{1,2} allowing the IL to be designed for a specific purpose. This tunability, in conjunction with their low vapour pressure,³ has seen ILs investigated for many applications, including gas chromatography,⁴⁻⁶ and gas separation and transport.^{7,8} As these applications are governed by processes at the air interface, a detailed understanding of the arrangement of surface ions and how this organisation influences interfacial properties is required. Surface properties may be manipulated via structural variation of the ions or the use of surface active species. In this manuscript we use neutron reflectivity and surface specific vibrational sum frequency spectroscopy (VSFS) to investigate the morphology of surfactants adsorbed at the ethylammonium nitrate (EAN) – air interface.

There are no previous reports of adsorbed surfactant structure at an IL surface. However, while investigating the formation of micelles in EAN, Evans *et al.*⁹ reported that various surfactants could decrease the surface tension from that of pure EAN (46.6 mN.m⁻¹), to a limiting value between 27.5 and 35.6 mN.m⁻¹ at the critical micelle concentration (cmc). While confirming surfactants adsorb at the EAN - air interface, no information concerning the adsorbed morphology was obtained.

Conversely, surfactant adsorbed layer structure at the air - water interface has been extensively studied.¹⁰⁻²⁰ As surfactants dissolved in both EAN and water self-assemble into surfactant micelles,^{9,21} lyotropic liquid crystals,²² microemulsions,²³ and adsorbed aggregates²⁴ with similar structures, it is likely that dissolved surfactants will form an oriented adsorbed monolayer at the surface of EAN, just as they do in aqueous solution. Published results for

surfactant structures at the air – water interface will provide a framework for interpreting our data.

At the air – water interface, the surface excess and area per molecule, the position of surfactant head and tail groups (and their thicknesses normal to the interface), and the number of solvent molecules associated with each adsorbed surfactant have been determined with precision using neutron reflectivity.^{10-12,16,17} The adsorbed layer structure of nonionic surfactants is a function of the surfactant concentration, the alkyl and ethoxy chain lengths, and temperature. Increasing surfactant concentration increases the thickness of the alkyl chain and ethoxy headgroup layers while decreasing the number of water molecules associated with each surfactant,¹¹ and the area per surfactant molecule decreases, reaching a limiting value at the cmc. Increasing the length of the surfactant alkyl chain causes the tailgroup layer thickness to increase,¹⁷ while an increase in the ethoxy chain length results in a thickening of the headgroup layer¹⁰ and increases the number of associated water molecules. The area per surfactant molecule decreases with longer alkyl chains,¹⁷ as longer hydrocarbon tails are more hydrophobic, leading to higher surface activity and stronger associations between surface adsorbed monomers. The area per surfactant molecule increases with ethoxy headgroups¹⁰ due to steric repulsions. Increasing the temperature affects surfactant behavior in two ways: alkyl chains become more soluble in water decreasing the hydrophobic interactions which drive surface adsorption, and the ethoxy headgroups become dehydrated reducing the hydrophilicity.^{12,16} For short ethoxy chain surfactants (<6 ethoxy units), the increased solubility of the alkyl tail dominates, and surface adsorption decreases upon warming. For long ethoxy chains (>6 ethoxy units) head-group dehydration dominates and increased adsorption results.¹⁶

Nonionic surfactant adsorption at the air - water interface has also been investigated using VSFS.¹⁹ The appearance of CH₃ peaks in the C₁₂E₅ – water VSFS spectrum at 0.1 μM shows that

adsorption commences far below the cmc (cmc = 71 μM). The CH_3 peaks do not intensify until the surfactant concentration reaches approximately 1.0 μM , suggesting the surfactant initially adsorbs with the alkyl chains orientated close to the plane of the surface, but as the surfactant concentration is increased the alkyl chains adopt a more upright position. Concurrently, the intensity of the bonded OH band at 3400 cm^{-1} increases, indicating ordered water molecules are hydrating the ethoxy head group. Selective deuteration of the surfactant tail group allowed the head group CH_3 contribution to the VSFS spectrum be ascertained. As no resonant features were noted, the headgroup is randomly oriented.

In this work we investigate the structure of nonionic polyoxyethylene alkyl ether surfactants (C_{12}E_4 , C_{14}E_4 , C_{16}E_4) adsorbed at the EAN – air interface. Variation in the surfactant alkyl chain length, concentration and temperature on adsorbed layer morphology is assessed.

2. Materials and Methods

Ethylammonium nitrate (EAN) was prepared by the slow addition of a nitric acid (Merck) aqueous solution to an ethylamine (Aldrich) aqueous solution in equimolar amounts.⁹ The temperature was maintained below 10°C. Water was removed from the EAN by rotary evaporation. The EAN was then purged with nitrogen and heated to 105-110°C to remove the final traces of water.²⁵ This led to water contents undetectable by Karl-Fischer titration. Deuterated EAN was prepared by the same process, however, after heating the EAN was mixed with D_2O (Aldrich) in a 3:1 ratio for several hours. The solution was then re-dried following the rotary evaporation, purging and heating steps. This resulted in, on average, 2.5 of the amino hydrogens being replaced with deuterium.

Tail deuterated nonionic polyoxyethylene alkyl ether surfactants (C_{12}E_4 , C_{14}E_4 , C_{16}E_4) were purchased from R.K. Thomas, University of Oxford, UK. The surfactants were dried in a

vacuum oven prior to use. The hydrocarbon tail was deuterated to provide contrast with the ethoxy headgroup. Hydrogenated tetraethylene glycol monotetradecyl ether ($C_{14}E_4$) was purchased from Nikkol and was used as received.

Neutron reflectivity measurements were conducted using the SURF reflectometer on the ISIS pulsed neutron source at the Rutherford-Appleton Laboratory, Didcot, United Kingdom. The measurements were made in the Q range 0.048 to $0.5 \text{ \AA}^{-1}$, at an angle of incidence of 1.5° . All experiments were performed in a nitrogen atmosphere. The reflectivity data was normalized using a scale factor determined from the reflectivity of D_2O , background normalization was completed for each measurement.

A detailed description of the VSFS spectrometer used for these experiments has been provided previously.²⁶ A brief summary of the experimental setup is given here. A pulsed picoseconds laser (Ekspla) provides the 1064 nm beam to the Optical Parametric Generator/Optical Parametric Amplifier (OPA/OPG), which in turn generates both the fixed visible and tunable infrared beams. Solutions of surfactant dissolved in EAN were measured in a closed glass/Teflon cell where the environment and temperature can be controlled. During all measurements a continuous nitrogen gas flow was maintained to prevent water ingress. The collected sum frequency beam passes through a photomultiplier, a monochromator, a gate integrator and then is analyzed by a computer.

3. Background Theory and Data Analysis

Neutron reflectivity

In specular reflectivity techniques a beam of neutrons is directed at the interface at an incident angle, θ . The reflected beam intensity, R , is measured as a function of the change in

momentum transfer, $Q = \frac{4\pi\sin\theta}{\lambda}$, normal to the surface, where λ is the neutron wavelength. The reflected intensity is a function of the scattering length density, $\rho = \sum_i n_i b_i$, where n_i is the number density of each component and b_i is its scattering length. The neutron scattering length densities for the species examined in this work are given in Table 1.

The differences between the scattering length densities of hydrogen (small and negative) and deuterium (large and positive), means that selective deuteration allows certain parts of molecules or ions to be highlighted. In aqueous systems, any contribution of the solvent to reflectivity can be masked by preparing “null reflective water”, in which the appropriate amounts of H₂O and D₂O are mixed to match the solvent scattering length density to air. This can not be achieved with EAN, as both deuterated and hydrogenated EAN have positive scattering length densities (Table 1).

Table 1: Calculated neutron scattering length densities (ρ), volumes and extended lengths of the surfactant head and tail groups, and hydrogenous and partially deuterated EAN.

	ρ ($\times 10^{-6} \text{ \AA}^{-2}$)	Volume ($\text{\AA}^3$)	Extended Length ($\text{\AA}$)
C₁₂D₂₅	7.04	350.2 ^a	16.68 ^a
C₁₄D₂₉	7.09	404 ^a	19.21 ^a
C₁₆D₃₃	7.13	457.8 ^a	21.47 ^a
(OC₂H₄)₄OH	0.74	253.3 ^b	14.4 ^b
C₂H₅ND₃NO₃	3.38	150 ^c	5.3 ^d
C₂H₅NH₃NO₃	1.30	150 ^c	5.3 ^d

a from ref ²⁷; b from ref ²⁸; c calculated from liquid density; d calculated by taking the cube root of the molecular volume²⁹

The neutron reflectivity data was modeled using the MOTOFIT³⁰ analysis package, which uses the Abeles matrix method.^{31,32} Each model contains the following five variables as a minimum: instrumental scale factor, scattering length densities of the solvent and the gas phase,

sample background, and the roughness of the solvent surface. As the reflectivity data is modeled, the thickness, scattering length density and roughness of each layer is allowed to vary within physically reasonable ranges. Reflectivity curves with multiple contrasts are fit simultaneously to a single model film structure, and the number of interfacial layers (between air and bulk IL) increased until an adequate physical description is realized.

Vibrational Sum Frequency Spectroscopy

A more thorough description of the theory behind vibrational sum frequency spectroscopy (VSFS) is provided in our previous paper.³³ Briefly, VSFS provides information about the first few molecular layers of an interface that have orientation different to the underlying (centrosymmetric) bulk medium. Two laser beams, one fixed visible beam and one tunable infrared beam, are overlapped on the surface of interest, interacting with surface molecules to generate a third beam. The intensity of the generated beam (I_{SFG}) is proportional to the intensities of the two incoming beams (I_{VIS} and I_{IR}) and the square of the second order nonlinear susceptibility $\chi^{(2)}$ which carries information about the interfacial moieties:

$$I_{SFG} \propto \left| \chi_{eff}^{(2)} \right|^2 I_{IR} I_{VIS} \quad (1)$$

Experiments using different polarization combinations either parallel (P) or perpendicular (S) to the plane of the interface of the of the sum frequency, visible, and infrared beams allow the elements of the nonlinear susceptibility $\chi^{(2)}$ tensor to be assessed. There are only four polarization combinations that give non-zero sum frequency signals for isotropic liquid interfaces: SSP, SPS, PSS and PPP.

In order to extract the amplitudes of the peaks present in the collected sum frequency spectrum, a custom IgorTM program is used, assuming a Lorentzian intensity profile:

$$I(\omega_{SF}) = \left| A_{NR} + \sum_{\nu} \frac{A_{\nu}}{\omega_{\nu} - \omega_{IR} - i\Gamma_{\nu}} \right|^2 \quad (2)$$

where A_{NR} refers to the nonresonant contribution to the SF signal, A_{ν} is the amplitude and ω_{ν} the wavelength of the ν^{th} vibrational mode, ω_{IR} is the frequency of the IR beam, and Γ_{ν} is the damping constant.

4. Results and Discussion

Neutron Reflectivity of Adsorbed Surfactants

Neutron reflectivity profiles for 1.0 wt% $C_{12}E_4$, $C_{14}E_4$, and $C_{16}E_4$ adsorbed at D-EAN – air and H-EAN – air interfaces are shown in Figure 1. At 1 wt% solution, these three surfactants are all above their respective critical micelle concentrations (cmc) in EAN, as determined by small angle neutron scattering.²¹ Hence the adsorbed layers examined here represent saturated surface films with micelles present in the liquid subphase. In H-EAN, the scattering length densities of the head group and solvent are nearly equal, so that the reflectivity is primarily a consequence of the deuterated tail layer. In D-EAN, the contrast between the head groups and the solvent gives rise to a second contrasting layer, and overall an apparently thicker film at the interface.

Figure 1: Neutron reflectivity profiles for $C_{12}E_4$ in $\blacktriangle$ H-EAN and $\triangle$ D-EAN, $C_{14}E_4$ in $\bullet$ H-EAN and $\circ$ D-EAN, and $C_{16}E_4$ in $\blacksquare$ H-EAN and $\square$ D-EAN at room temperature. The parameters used for the fits (solid line H-EAN, dashed line D-EAN) are summarized in Table 2. The data for the pure EAN interface (X) has been included for reference. The $C_{14}E_4$ and $C_{16}E_4$ data have been offset vertically by 0.5 and 1.0 for clarity.

These data cannot be fit using a single layer model. The data for the two scattering contrasts were simultaneously fit using a two layer model in which surfactant tail groups are oriented towards the gas phase and head groups towards the bulk liquid. The best-fit parameters obtained are summarised in Table 2. The tail group layer thickness increases by approximately 1.2 Å for each CH_2 unit, from 9.75 ± 0.25 Å for $C_{12}E_4$ to 12.0 ± 0.5 Å for $C_{14}E_4$ and 14.5 ± 0.5 Å for $C_{16}E_4$. This agrees well with expectations for an all-trans chain, 1.27 Å,²⁷ but is at odds with the overall thicknesses, which are consistent with surfactant tails oriented at an angle to the interface or containing many *gauche* conformers. Similar length scale changes have however been observed in (thicker) adsorbed layers of $C_{12}E_6$ and $C_{14}E_6$ at air - water interfaces.^{17,28}

Surface roughness has two key components: the static distribution of interfacial molecules and thermal capillary waves. Surface roughness increases the effective thickness of interfacial layers.¹¹ To provide the most accurate possible description of the adsorbed layer the effect of roughness is accounted for by fitting routines. In this work roughness values were constrained between 4 – 6 Å (the roughness determined for the pure EAN interface), which is slightly lower than values reported in aqueous systems, e.g. 8.4 Å for C₁₂E₄.¹²

Table 2: Fitted and derived parameters for C₁₂E₄, C₁₄E₄, C₁₆E₄ adsorbed layers at the air - EAN interface. Comparable data for films adsorbed at air - water interfaces also shown

Surfactant	Conc. (wt%)	Thickness Tail Group Layer (Å)	ρ_{tail} ($\times 10^{-6} \text{ Å}^{-2}$)	Roughness Tail Group Layer (Å)	Thickness Head Group Layer (Å)	ρ_{EO} ($\times 10^{-6} \text{ Å}^{-2}$)	Roughness Head Group Layer (Å)	a_0 (Å ²)	solvation number
25°C									
C ₁₂ E ₄	1.0	9.8 ± 0.25	5.0 ± 0.1	4.0 ± 0.1	7.4 ± 0.2	1.5	6.0 ± 0.1	48.3 ± 0.3	0.7
C ₁₄ E ₄	1.0	12.0 ± 0.5	5.1 ± 0.1	4.6 ± 0.1	7.4 ± 0.2	1.5	6.0 ± 0.1	47.5 ± 1.3	0.7
C ₁₆ E ₄	1.0	14.5 ± 0.5	5.1 ± 0.1	4.4 ± 0.1	8.0 ± 0.3	1.5	6.0 ± 0.1	44.5 ± 0.9	0.7
C ₁₂ E ₄	0.1	7.0 ± 0.5	6.8 ± 0.2	4.0 ± 0.1	5.7 ± 0.3	1.0 ± 0.1	6.0 ± 0.1	52.0 ± 2.2	0.25
60°C									
C ₁₂ E ₄	1.0	9.75 ± 0.25	5.3 ± 0.2	4.5 ± 0.1	7.0 ± 0.2	1.3 ± 0.1	5.9 ± 0.1	48.9 ± 0.9	0.7
C ₁₄ E ₄	1.0	11.5 ± 0.5	5.3 ± 0.1	5.6 ± 0.1	7.0 ± 0.2	1.4 ± 0.1	5.4 ± 0.1	46.8 ± 0.6	0.7
C ₁₆ E ₄	1.0	16.8 ± 0.5	4.6 ± 0.2	6.0 ± 0.1	10.8 ± 1.4	2.1 ± 0.1	5.1 ± 0.1	48.9 ± 0.9	1.3
Water (25°C)									
C ₁₂ E ₃	5.5 × 10 ⁻⁵ M	16.5 ± 1	-*	-	10.7 ± 1	-	-	37.0 ± 2	6
C ₁₂ E ₃	0.3 × 10 ⁻⁵ M	14.0 ± 1	-	-	8.5 ± 1	-	-	64.0 ± 4	9
C ₁₂ E ₄ ¹⁰	6.9 × 10 ⁻⁵ M	12.0 ± 1.0	-	-	11.0 ± 1.0	-	-	44.0 ± 1.0 (42.0) ³⁴	7
C ₁₂ E ₆ ²⁸	8.0 × 10 ⁻⁵ M	16.0 ± 1.0	-	-	16.5 ± 1.0	-	-	55.0 ± 3.0	10
C ₁₄ E ₆ ¹⁷	1.0 × 10 ⁻⁴ M	19.0 ± 1.0	-	-	17.0 ± 1.0	-	-	50.0 ± 2.0	-

*not reported

The molecular areas at the EAN-air interface are $48.3 \pm 0.3 \text{ \AA}^2$ for C_{12}E_4 , $47.5 \pm 1.3 \text{ \AA}^2$ for C_{14}E_4 , and $44.5 \pm 0.9 \text{ \AA}^2$ for C_{16}E_4 . For C_{12}E_4 , this is somewhat larger than either the $44.0 \pm 1.0 \text{ \AA}^2$ found by neutron reflectivity¹⁰ or $42.0 \text{ \AA}^2$ derived from surface tensiometry³⁴ at the air – water interface. Longer alkyl tails increase surfactant solvophobicity, resulting in higher saturated adsorption densities at the EAN – air interface and lower molecular area. A similar effect is observed in aqueous systems, as can be seen by comparing e.g. C_{12}E_6 and C_{14}E_6 (Table 2).

These molecular areas are somewhat smaller than the $52.2 \pm 1.5 \text{ \AA}^2$ found by small-angle x-ray scattering for C_{14}E_4 in EAN-alkane microemulsions.²³ A larger molecular area of $53.8 \text{ \AA}^2$ was also found by SANS³⁵ for aqueous C_{12}E_4 microemulsions than at the air-water interface. Therefore, it is reasonable that the area per molecule at the EAN - air interface is lower than at the EAN – alkane interface.

The thickness of the polar head group layer is found to be $7.4 \pm 0.2 \text{ \AA}$ for C_{12}E_4 and C_{14}E_4 , and $8.0 \pm 0.3 \text{ \AA}$ for C_{16}E_4 . As a C_{16}E_4 monomer occupies a smaller area at the interface than C_{12}E_4 and C_{14}E_4 (as more surfactant is adsorbed), the slight increase in head group layer thickness is due to increased steric interactions between ethoxy chains. From the fitted scattering length density the number of solvent ions associated with each surfactant can be calculated (Table 2). For the E_4 head groups investigated here, this yields 0.7 EAN ion pairs associated with each head group independent of alkyl chain length. (Even if EA^+ is the only species in the head group film there are still less than two EA^+ per surfactant monomer).

Effect of Surfactant Concentration

Neutron reflectivity profiles for 0.1 wt% C_{12}E_4 , C_{14}E_4 , and C_{16}E_4 adsorbed at the D-EAN – air interface are shown in Figure 2 and the fitted parameters are summarised in Table 2. Within experimental uncertainty, there is no difference between the reflectivity curves for C_{14}E_4

and C₁₆E₄ at 0.1 wt% and 1.0 wt%, and the data is fit using the same model as for 1.0 wt%. This is expected, as both solutions remain above their cmc after dilution. However, clear differences in reflectivity are seen for C₁₂E₄ when its concentration is decreased below its cmc (approx. 0.8 wt%²¹) to 0.1 wt%, and modelling reveals a decrease in the alkyl chain layer thickness, from 9.75 ± 0.25 Å at 1.0 wt% to 7.0 ± 0.5 Å. Both the scattering length density of the alkyl tail and the area per molecule are higher at the lower concentration, so the hydrophobic layer is thinner and a denser alkane region. A similar effect has been observed at the air-water interface, where the alkyl layer became 2.5 Å thinner when the C₁₂E₃ was diluted from its cmc (5.5×10^{-5} M) to 0.3×10^{-5} M.¹¹ In both cases the reduced alkyl layer thickness results from decreased surfactant adsorption such that surfactant tail groups are less sterically confined by their neighbours and orientated on average closer to the interfacial plane.

The ethoxy chain layer of C₁₂E₄ also becomes thinner at lower concentration, consistent with an increase in the area per molecule (Table 2). At the lower concentration fewer molecules are adsorbed at the interface, reducing steric interactions between the head groups. Surprisingly, there are fewer solvent ions associated with each surfactant at 0.1 wt% (0.25 ion pairs) compared to 1.0 wt% (0.7 ion pairs). This also differs from aqueous systems, where the number of associated water molecules increases from 7 to 9 when the concentration of C₁₂E₄ was decreased from 6.9×10^{-5} M to 1.8×10^{-5} M.¹⁰ This strengthens our picture of a compact, poorly-solvated ethoxy chain layer at the EAN – air interface, which extends into solution only as a result of lateral crowding by adsorbed neighbours – more so for the more strongly adsorbed hexadecyl homologue, and contrasts starkly with good solvation in aqueous systems. In EAN, not only are alkanes less solvophobic, ethylene oxide oligomers are apparently less solvophilic.

Figure 2: Neutron reflectivity profiles for $C_{12}E_4$ at $\blacktriangle$ 0.1 wt% and $\triangle$ 1.0 wt%, $C_{14}E_4$ at $\bullet$ 0.1 wt% and $\circ$ 1.0 wt%, and $C_{16}E_4$ at $\blacksquare$ 0.1 wt% and $\square$ 1.0 wt% in D-EAN at room temperature. The parameters used for the fits (solid line 0.1 wt%, dashed line 1.0 wt%) are summarized in Table 2. The $C_{14}E_4$ and $C_{16}E_4$ data have been offset for clarity.

Inset: scattering length density profiles of 0.1 wt% (solid line) and 1 wt% (dashed lined) $C_{12}E_4$.

Effect of Temperature

Neutron reflectivity profiles for 1.0 wt% $C_{12}E_4$, $C_{14}E_4$, and $C_{16}E_4$ adsorbed at the D-EAN – air interface at 60°C are presented in Figure 3. For both $C_{12}E_4$ and $C_{14}E_4$ the alkyl chain thickness is constant, and there is a decrease in the ethoxy chain layer thickness on warming at the limit of resolution, from 7.4 ± 0.2 Å to 7.0 ± 0.2 Å. By contrast, the reflectivity data for $C_{16}E_4$ changes substantially with temperature, increasing the thickness of both the tail (from 14.5 ± 0.5 Å to 16.8 ± 0.5 Å) and head group layers (8.0 ± 0.3 Å to 10.9 ± 1.3 Å). The adsorption density is higher indicating lower solubility of the amphiphile in EAN, and the area per molecule decreases to 41.6 ± 0.6 Å². Solvent ions are more able to penetrate this extended head group

chain and the number of EAN ion pairs solvating each surfactant headgroup increases from 0.7 to 1.3. This result differs from aqueous systems, where solvent penetration decreases with temperature,¹² which suggests that the thickness of the head group layer is more strongly determined by solvation in water, whereas in EAN steric interactions between head groups of adsorbed monomers are more important.

Figure 3: Reflectivity (log) profiles for $C_{12}E_4$ at $\blacktriangle$ 60°C and $\triangle$ room temperature, $C_{14}E_4$ at $\bullet$ 60°C and $\circ$ room temperature, and $C_{16}E_4$ at $\blacksquare$ 60°C and $\square$ room temperature in D-EAN at 1.0 wt%. The parameters used for the fits (solid line 60°C, dashed line room temperature) are summarized in Table 2. The $C_{14}E_4$ and $C_{16}E_4$ data have been offset for clarity. Inset: scattering length density profiles of $C_{16}E_4$ at 60°C (solid line) and 25°C (dashed lined).

Vibrational Sum Frequency Spectroscopy of Adsorbed Surfactants

VSFS provides information concerning the structure adopted by nonionic surfactants at the EAN – air interface that cannot be resolved using neutron reflectivity. Here we focus on

C₁₄E₄ as a representative surfactant, and to enable comparison with previous work which has characterized the structure of micelles²¹ and microemulsions²³ in EAN. VSFS spectra were recorded in three wavenumber regions. The use of tail deuterated surfactant allows the contribution to the spectrum by EA⁺ alkyl chains and surfactant ethoxy groups to be highlighted, as CD and CH vibrational modes appear in different wavenumber regions. The 2700 – 3200 cm⁻¹ region provides information on the CH stretching vibrations of the EAN cation alkyl chains, and hydrogenous methylene groups of the h-C₁₄E₄ ethoxy head and tails, and d-C₁₄E₄ ethoxy headgroups, as well as the NH stretching of EAN. 1000 – 1600 cm⁻¹ is the CO stretching range, where contributions from surfactant headgroups only are present.

Figure 4a shows the SSP polarization spectra in the CH region for the interface between air and pure EAN, and between air and a 1 wt% d-C₁₄E₄ – EAN solution. There are four main peaks in the pure EAN spectrum, three of these are assigned to CH₃ stretching modes: symmetric CH mode of the CH₃ group at 2890 cm⁻¹, a Fermi Resonance of the symmetric CH mode of the CH₃ group at 2945 cm⁻¹, and antisymmetric CH₃ stretch at 2989 cm⁻¹. The fourth peak at 3114 cm⁻¹ is the symmetric NH₃ stretch.³³ The pure EAN CH₃ peak intensities are approximately 8 times weaker after surfactant adsorption. This may be a consequence of either a decrease in the number of interfacial species that generate the signal, a change in the orientation of the interfacial species, or some combination of both. The constant intensity ratio of the Fermi resonance CH₃ symmetric peak (2945 cm⁻¹) to the CH₃ symmetric peak (2890 cm⁻¹) before and after surfactant adsorption suggests that the orientation of the interfacial EAN is not significantly affected by surfactant adsorption. Therefore, the decrease in signal strength is primarily due to adsorbing surfactant displacing the EAN from the interface. This is consistent with EAN only slightly solvating the ethylene oxide layer, as suggested by neutron reflectivity.

Figure 4: a) SSP spectra of the EAN – air interface and 1 wt% d- $C_{14}E_4$ adsorbed at EAN – air interface; b) SSP, PPP and SPS spectra of d $C_{14}E_4$ adsorbed at the EAN – air interface in CO region (spectra are offset for clarity); c) SSP spectrum of the EAN – air interface and 1 wt% h- $C_{14}E_4$ adsorbed at the EAN – air interface. (The intensities in a) and c) are normalized to the most intense peak and are not comparable between figures.)

Interfacial EA⁺ peaks in the PPP (2945 and 2989 cm⁻¹) and the SPS (2985 cm⁻¹) spectra became less distinct in the presence of 1wt% d-C₁₄E₄ (not shown). It appears that CD vibrational modes associated with the surfactant tailgroup interfere with the EAN CH stretches,³⁶ causing the peaks to shift and change shape. Overlapping vibrational modes can interfere with the VSFS spectrum constructively or destructively, depending on their phase. Both effects cause the spectral features to change, which prevents us from performing orientation analysis on interfacial EAN after surfactant addition.

Figure 4b shows the CO spectral region of 1wt% d-C₁₄E₄ in EAN under different polarizations, which has no well resolved features, except for a broad band at lower wavenumbers in the SSP spectrum due to nonresonant background. This indicates the surfactant ethoxy headgroup has no preferred orientation.

The VSFS spectrum of 1wt% hydrogenated C₁₄E₄ adsorbed at the EAN – air interface is shown in Figure 4c. The most noteworthy difference between this spectrum and that of pure EAN is the dominant symmetric CH₂ stretching peak at 2860 cm⁻¹. The appearance of this peak indicates a significant number of gauche defects within the hydrocarbon layer consistent with conformational disorder, as the CH₂ groups in an all-*trans* configuration are in a locally centrosymmetric environment rendering them VSFS inactive.¹⁸ This is similar to results for nonionic surfactant adsorption at the air – water interface.^{14,19}

The emergence of a CH₂ stretching frequency in the VSFS spectrum of C₁₄E₄ confirms that gauche conformers rather than a tilted all-*trans* alkyl tail of the adsorbed surfactant are responsible for the unexpectedly small layer thicknesses measured by neutron reflectometry. For example neutron reflectivity studies of C₁₂E₄ adsorbed at the air – water interface¹⁰ yield a layer thickness of 12.0 ± 1.0 Å, compared with 9.8 ± 0.3 Å in EAN (Table 2). As noted above, the

film thickness increases with increasing chain length as though an all-*trans* segment was being inserted.

Overall this generates a picture of an adsorbed layer comprised of a compact and tightly-packed layer of ethylene oxide marginally penetrated by solvent, consistent with results obtained for polyoxyethylene micelles in EAN.²¹ By contrast, the surfactant head group layer in aqueous systems is both thicker and more highly solvated (11 Å, and 7 water molecules per C₁₂E₄ head group).¹⁰ As a result, surfactant tails adopt a more upright orientation at the water surface to minimize contact with the polar subphase and solvated head group layer. As surfactant molecules have much higher solubility in EAN than water (surfactant cmc's are orders of magnitude higher in EAN),⁹ surfactant tail groups are much less strongly repelled from the head group layer.

4. Conclusions

Nonionic polyoxyethylene alkyl ether surfactants (C₁₂E₄, C₁₄E₄, C₁₆E₄) adsorb as an oriented monolayer at the EAN - air interface, forming a saturated film above their critical micelle concentrations, exhibiting many similarities with aqueous systems. At room temperature, the thickness of the tail group layer increases with the length of the surfactant tail groups. The head group layer thickness is essentially constant for C₁₂E₄ and C₁₄E₄, but increases for C₁₆E₄, due to a higher adsorption density resulting in stronger steric interactions between neighbouring ethoxy chains. However, the headgroup and tail layers are both thinner than at the air – water interface. The polar headgroup layer is poorly solvated by, on average, less than one EAN ion pair per surfactant monomer.

When the C₁₂E₄ concentration is reduced well below its cmc to 0.1 wt%, the adsorption density decreases, and both the head group and tail layers become thinner and more compact,

with the alkyl chains orientated closer to the plane of the interface. In contrast with water, less EAN is incorporated into the head group layer. No change in the C₁₄E₄ or C₁₆E₄ adsorbed layer morphology is seen over the same concentration range, as both remain above or near their cmcs.

When temperature is increased to 60°C the overall C₁₆E₄ adsorbed layer becomes thicker, but no change in morphology is observed for C₁₂E₄ and C₁₄E₄. Warming reduces the solubility of C₁₆E₄, increasing the surface excess (reducing the area per molecule), and resulting in both the alkyl and ethoxy chains extending out from the interface. This also allows more EAN to penetrate the film, increasing solvation of the surfactant headgroup. These results suggest that there is little change in the solubility of C₁₂E₄ and C₁₄E₄ up to 60°C.

VSFS shows a decrease in signal strength from EAN when C₁₄E₄ is added, indicating that EAN is displaced by surfactant adsorption. A CH₂ vibrational mode dominates the CH spectral range revealing the presence of gauche conformers in the surfactant hydrocarbon tail, which is collapsed slightly towards the interface relative to its all-*trans* extended length. The lack of features in the CO region confirms that the surfactant headgroups have no preferred orientation in the adsorbed layer.

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